

Table I. Product Distribution for the Bimolecular Reaction of Secondary Alkyl Derivatives with Alkoxides

Alkyl X	X	Base	Solvent	Olefins produced, %		
				1	<i>cis</i> -2	<i>trans</i> -2
2-Butyl	Cl	KO- <i>t</i> -Bu	<i>t</i> -BuOH	67	14	18
	Br	KO- <i>t</i> -Bu	<i>t</i> -BuOH	54	19	27
	I	KO- <i>t</i> -Bu	<i>t</i> -BuOH	33	21	46
	Tos	KO- <i>t</i> -Bu	<i>t</i> -BuOH	62	24	14
	Tos	KOEt	EtOH	32	24	44
2-Pentyl	Tos	KO- <i>t</i> -Bu	<i>t</i> -BuOH	74	18	8
3-Pentyl	Tos	KO- <i>t</i> -Bu	<i>t</i> -BuOH		65	35
	Tos	NaOEt	EtOH		30	70
	Tos	NaO- <i>i</i> -Pr	<i>i</i> -PrOH		40	60
	Tos	KO- <i>t</i> -Bu	THF		31	69
	Tos	KO- <i>t</i> -Bu	Diglyme		30	70
<i>trans</i> -2-Methylcyclohexyl	Tos	KO- <i>t</i> -Bu	<i>t</i> -BuOH	1 ^a	99 ^b	
<i>trans</i> -2-Methylcyclopentyl	Tos	KO- <i>t</i> -Bu	<i>t</i> -BuOH	1 ^c	99 ^d	

^a 1-Methylcyclohexene. ^b 3-Methylcyclohexene. ^c 1-Methylcyclopentene. ^d 3-Methylcyclopentene.

pentene. Finally, 3-pentyl tosylate yields 65% *cis*-2- and 35% *trans*-2-pentene.

All three components, arenesulfonate as the leaving group, *t*-butoxide as the base, and *t*-butyl alcohol as the solvent, appear to be required to achieve this formation of the *cis* alkene. Thus use of the halide in the elimination gives the usual preferred *trans*. The use of potassium ethoxide in ethanol on the tosylate yields predominantly *trans*. Even the use of potassium *t*-butoxide in tetrahydrofuran or diglyme on the tosylate gives predominant *trans*. Finally, the treatment of *trans*-2-methylcyclohexyl tosylate with potassium *t*-butoxide in *t*-butyl alcohol yields 99% 3-methylcyclohexene. Thus, this reaction reveals the usual stereochemical preference for *trans* E2 elimination.

These results are summarized in Table I.

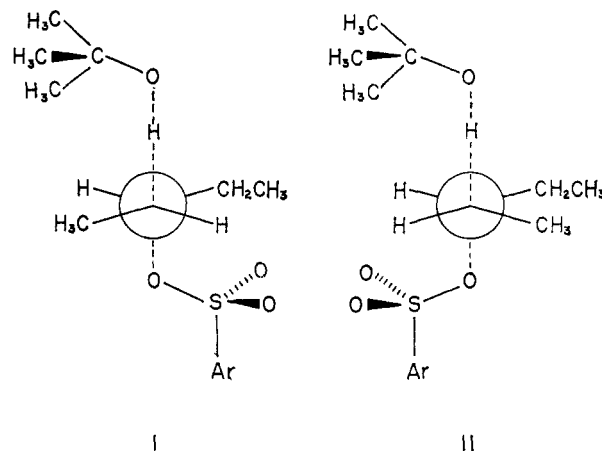
We wish to suggest that the steric model for E2 eliminations^{4,5} provides a possible explanation for this unusual formation of *cis* olefin. According to this interpretation the preferred formation of the *cis* isomer in the present reaction is a consequence of the fact that the large steric requirements of both the leaving arenesulfonate group and the solvated *t*-butoxide base cause transition state II to be more favorable energetically than transition state I.

In the usual elimination reaction, the steric interactions between the two alkyl groups (ethyl and methyl in I and II) apparently cause transition state I, with its alkyl groups separated, to be preferred. In the present case, it is our suggestion that the combined presence of two large, sterically demanding groups alters this situation. The geometrical requirements of both groups is such that they must project to the side of the two bonds undergoing rupture.

In a conformation in which the two alkyl groups are to enjoy the separation provided by a *trans* arrangement, there would appear to be two major possibilities for the attacking *t*-butoxide and departing arenesulfonate groups. They can either project in opposite directions

(4) H. C. Brown and I. Moritani, *J. Am. Chem. Soc.*, **78**, 2203 (1956).

(5) H. C. Brown and R. L. Klimisch, in press.



(as shown in I) or they could project in the same direction. In either case there will be significant steric interactions between the alkyl groups and these large, bulky moieties. It is our proposal that the system can reduce the steric interactions by allowing the two alkyl groups their relatively minor interactions in favor of giving the arenesulfonate and *t*-butoxide groups greater freedom on the opposite side of the assembly (II).

Irrespective of whether this interpretation provides the final explanation for this interesting phenomenon,⁶ it is becoming evident that the direction of elimination is subject to a remarkably wide range of control² not envisaged in the original interpretation.⁷

(6) It has proven possible to incorporate the interesting results with the onium salts (ref. 3) into the same model. This extended interpretation will be reported shortly.

(7) M. L. Dhar, E. D. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw, and L. I. Woolf, *J. Chem. Soc.*, 2093 (1948).

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The Preparation and Properties of Trimethylenecyclopropane

Sir:

We wish to report the formation of trimethylenecyclopropane (I). This hydrocarbon has been the subject of much speculation with respect to its stability,^{1,2} and a recent report has described the isolation and characterization of the remarkably stable trisopropylidenecyclopropane.³ The parent hydrocarbon, representing an excellent example of a completely cross-conjugated system and having a distinct relationship to benzene (same number of carbon and hydrogen atoms, same degree of unsaturation, and an expected planar structure), has never been prepared.⁴

Compound I was obtained from 2,3-bis(bromomethyl)-1-methylenecyclopropane (IV) which in turn was prepared from the reduction product⁵ of Feist's acid (II). The dibromide, obtained in yields ranging

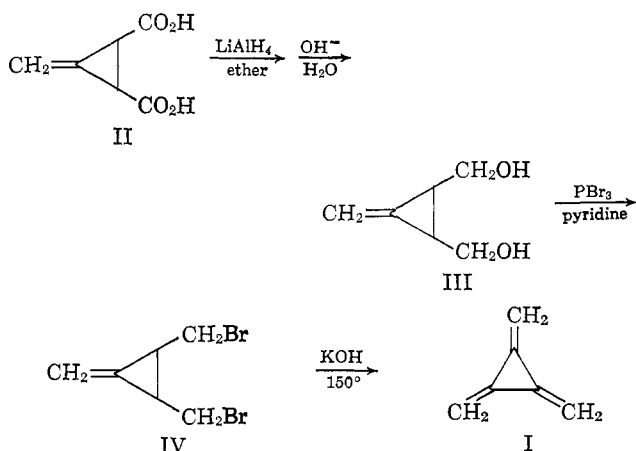
(1) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(2) M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 692 (1965).

(3) G. Köbrich and H. Heinemann, *Angew. Chem.*, **77**, 590 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965).

(4) (a) A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **81**, 1212 (1959); (b) I. A. D'Yakonov and E. M. Khoricheva, *Zh. Obshch. Khim.*, **34**, 2802 (1964).

(5) W. G. Brown and E. A. Dorko, unpublished results. See E. A. Dorko, Ph.D. Dissertation, University of Chicago, 1964.



from 30 to 45%,⁶ was characterized by its elemental analysis (Found: C, 30.36; H, 3.72; Br, 65.75) and infrared and n.m.r. spectra. The infrared shows a band at 1750 cm^{-1} characteristic for carbon-carbon double bond stretch in methylenecyclopropane compounds⁷ and a band at 905 cm^{-1} due to vinylic carbon-hydrogen out-of-plane vibrations.⁸ The n.m.r. spectrum consists of a triplet at τ 4.48 ($J = 1.8$ c.p.s., $\text{CH}_2=$),⁹ a doublet at τ 6.65 ($J = 5.0$ c.p.s., methylene protons), and a multiplet 110 c.p.s. downfield (internal TMS standard) due to the cyclopropyl protons. The ratio of areas was 1:2:1.

The dibromide IV was added dropwise to a U-tube filled with KOH heated to 150° through which a stream of helium was flowing. As the triene formed, it was swept into a series of cold traps by the helium stream and was condensed and solidified at -78°. The yield of I was 47% based on total bromide passed over the KOH.¹⁰

The mass spectrum of I, determined on a sample of the vapor, shows the 100% peak at m/e 78 (parent mass).¹¹ The cracking pattern is shown in Table I. A comparison was made with the cracking pattern of benzene.¹² Although the cracking pattern of I shows only one peak (at m/e 28) that is not present in the pattern for benzene, the relative intensities of the peaks for the two compounds are strikingly different. For example, while both show 100% peaks at m/e 78 the peak at m/e 52 for benzene has a relative intensity of 22.4 vs. 82.4 for I. A molecular weight determination by the mass spectral effusion method¹³ resulted in a

value of 75. This is within experimental error of the expected value of 78 and eliminates the possibility of a dimer of I.

Table I. Mass Spectrum of Trimethylenecyclopropane

m/e	Relative intensity	m/e	Relative intensity
12	1.9	48	0.7
13	1.2	49	6.6
14	3.2	50	50.2
15	1.9	51	71.7
24	0.6	52	82.4
25	2.2	53	8.0
26	14.1	61	2.9
27	17.6	62	3.7
28	22.6	63	12.1
36	5.6	73	2.1
37	10.8	74	7.2
37.5	2.9	75	2.9
38	13.8	76	6.7
38.5	1.1	77	44.6
39	41.6	78	100.0
40	3.1	79	18.1
41	4.7	80	3.2
43	2.0		

Further characterization of I was done spectroscopically. The infrared spectrum consists of relatively few bands¹⁴ with a strong one at 874 cm^{-1} (vinylic carbon-hydrogen out-of-plane vibrations⁶) and a weak one at 1773 cm^{-1} . (This band occurs in the same region as the carbon-carbon double bond stretching band in methylenecyclopropane.)⁷ The n.m.r. spectrum, obtained in CCl_4 , displays the expected single peak at τ 4.98. The n.m.r. spectrum for methylenecyclopropane is reported to display a quintuplet at τ 4.64.¹⁵ This comparison indicates that vinylic protons are indeed being observed. The ultraviolet spectrum, obtained with a sample of the vapor, shows a broad absorption with two maxima which occur at 213 (ϵ_{max} 19,400)¹⁶ and at 289 $\text{m}\mu$ (ϵ_{max} 3750).¹⁶ In ethanol solution the maxima occur at 213 and 295 $\text{m}\mu$. No fine structure is observed with either the vapor or the solution. As a comparison, the λ_{max} for triisopropylidenecyclopropane is reported to occur at 309.5 $\text{m}\mu$.³ The bathochromic shift is the expected effect of the methyl substituents on the double bond system.

The triene I is stable for a period of days at -78° and can be readily transferred on a vacuum line if the pressure is kept low. However, polymerization starts to occur when the vapor is warmed to room temperature. Polymerization proceeds through a colorless liquid to a viscous oil and finally to a yellow solid. A solution of the triene in CCl_4 on standing at 0° also produced the yellow polymer as a precipitate. The nature of this polymer is currently being studied in order to determine if polymerization is proceeding by way of a Diels-Alder mechanism.

Acknowledgment. The author wishes to thank Mr. O. H. Loeffler for allowing him to use the facilities of the Gorgas Laboratory, Rohm and Haas Company,

(6) Ya. M. Slobodin and I. N. Shokov, *Zh. Obshch. Khim.*, **21**, 2005 (1951)] report a similar yield of 1,1-dibromomethylcyclopropane by this procedure.

(7) (a) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and D. E. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953); (b) K. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 51.

(9) The coupling between protons four bonds removed in methylenecyclopropane has been observed and discussed for Feist's acid. For this discussion see J. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

(10) A small amount of starting material (less than 5% of the total amount reacted) was also recovered. It condensed in a cold trap at -40°.

(11) The spectrum was taken with a Consolidated Engineering Corp. Type 21-620 spectrograph operating at 100 v. I.P. The source temperature was maintained at 156°.

(12) The spectrum for benzene was obtained under identical conditions used with I. For the published spectrum of benzene see "Catalog of Mass Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., spectrum no. 175.

(13) (a) M. Eden, B. E. Burr, and A. W. Pratt, *Anal. Chem.*, **23**, 1735 (1951); (b) P. D. Zemany, *J. Appl. Phys.*, **23**, 924 (1952).

(14) The complete spectrum will be reported along with a theoretical analysis in another communication.

(15) B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962).

(16) The extinction coefficients are approximate since the pressure within the gas cell could only be determined roughly.

Huntsville, Ala., where a substantial portion of this work was performed.

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Racemization of Camphor during π -Sulfonation. Evidence for Exclusive *exo*-Methyl Migration

Sir:

Camphor-8-¹⁴C (I) was prepared by the following sequence of reactions: carbonation of sodio-3-methylnorbornan-2-one, using ¹⁴C-labeled carbon dioxide, followed by reaction with methylmagnesium iodide to give 2,3-dimethyl-3-hydroxynorbornane-2-carboxylic acid (II), which was separated from nonacidic material and rearranged by 85% sulfuric acid to 1,7-dimethylnorbornane-7-carbo-2-lactone (III, m.p. 192–193°, reported¹ 192–194°); lithium aluminum hydride reduction to 8-hydroxyisoborneol-8-¹⁴C (IV, m.p. 275–276°. Anal. Calcd. for C₁₀H₁₈O₂: C, 70.54; H, 10.66. Found²: C, 70.35; H, 10.58); Jones oxidation to 8-hydroxycamphor-8-¹⁴C (V, m.p. 232–233°; reported³ 233°); conversion to 8-bromocamphor-8-¹⁴C (VI, m.p. 120–122°, reported⁴ 121.5–122.5°); and hydrogenolysis to I-8-¹⁴C.

Sulfonation of I using chlorosulfonic acid⁵ afforded camphor-9-sulfonic acid (VIII)⁶ which is virtually completely racemized, even when starting with optically pure (+)-I.

Conversion of VIII to 9-bromocamphor (IX, m.p. 92–93°, reported⁵ 93–94°) was accomplished by means of phosphorus pentabromide and heat⁵; IX was converted partly to racemic I and partly to 9-hydroxycamphor (X, m.p. 233–234°, reported^{7,8} 233°). Oxidation of X afforded 1,7-dimethylnorbornan-2-one-7-*anti*-carboxylic acid (XI, m.p. 250–251°, reported 249–250°, ⁷ cf. footnote 6).

Degradation to provide removal of two of the three methyl groups of I (or XI) for determining isotope distribution was carried out on racemic I (from IX) (by reduction to isoborneol, dehydration *via* the phenylurethan to camphene, and isolation of formaldehyde (from original C-10) and dimethylnorcampholide by a previously published procedure⁹ and on XI using a modified Hunsdiecker reaction,¹⁰ which provided the original C-9 as carbon dioxide (trapped in phenylmagnesium bromide).

Using a liquid scintillation counter, half of the original radiocarbon was found in C-10 and half in C-8 (none in C-9).

(1) S. Beckmann and H. Geiger, *Ber.*, **92**, 2411 (1959).

(2) Spang Microanalytical Laboratory, Ann Arbor, Mich.

(3) Y. Asahina and M. Ishidate, *Ber.*, **67**, 71 (1934).

(4) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Am. Chem. Soc.*, **81**, 6305 (1959).

(5) F. A. Kipping and W. J. Pope, *J. Chem. Soc.*, **63**, 593 (1893); **67**, 155 (1895).

(6) The *anti* configuration is implicit in ref. 3 and 4. Explicitly we have demonstrated this by oxidizing lactone III to 1,7-dimethylnorbornan-2-one-7-*syn*-carboxylic acid (VII, m.p. 273–275°, reported 269–270°)⁷ which differs from the *anti* isomer XI.

(7) Y. Asahina and M. Ishidate, *Ber.*, **66**, 1673 (1933).

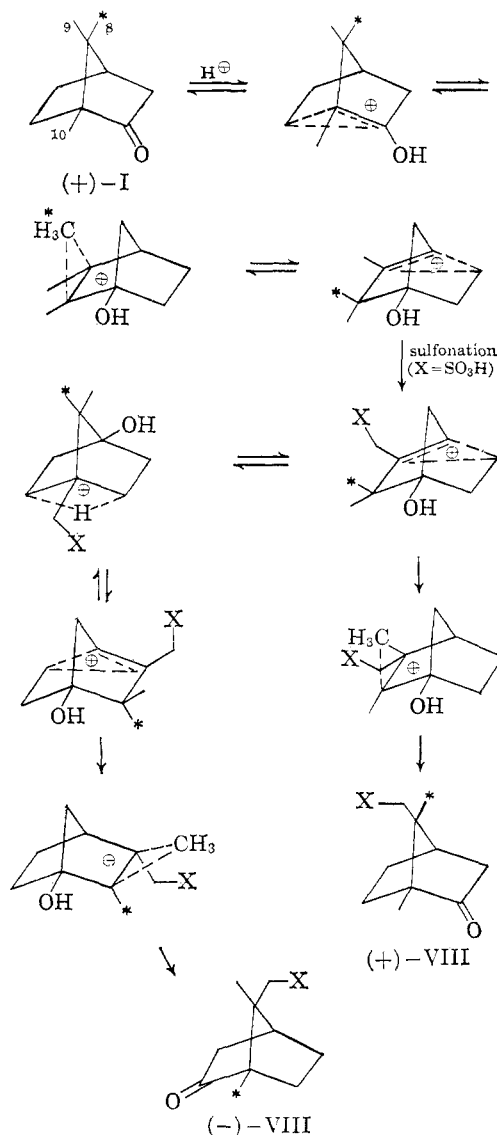
(8) R. C. Guha and S. C. Bhattacharyya, *J. Indian Chem. Soc.*, **21**, 261 (1944).

(9) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Am. Chem. Soc.*, **85**, 2282 (1963).

(10) S. J. Cristol and W. J. Firth, *J. Org. Chem.*, **26**, 280 (1961).

Next, labeled (\pm)-I was diluted with (+)-I, converted to the menthydrazone,¹¹ and recrystallized repeatedly until the specific radioactivity fell to slightly more than half the original value. (+)-Camphor-8-¹⁴C was then regenerated¹¹ and sulfonated, and the sulfonic acid was resolved¹² to give (+)-VIII. Degradation of (+)-VIII by the same procedures as before showed the label to be at C-8.

These data are consistent with a mechanism in which sulfonation is both preceded and followed by migrations involving *exo*-methyl to the exclusion of *endo*-methyl, *e.g.*



Furthermore, recovery of labeled, partially racemized I from an incomplete sulfonation experiment, followed by degradation to dimethylnorcampholide and formaldehyde, showed ¹⁴C distribution consistent with a similar racemization process without sulfonation (*i.e.*, omit sulfonation step and omit X from the structures). This, therefore, is also in keeping with exclusive *exo*-methyl migration.

Berson¹³ has recently presented a cogent argument in

(11) R. B. Woodward, T. P. Kohman, and G. C. Harris, *J. Am. Chem. Soc.*, **63**, 120 (1941).

(12) W. J. Pope and J. Read, *J. Chem. Soc.*, **97**, 992 (1910).

(13) J. A. Berson, R. G. Bergman, J. H. Hammons, A. W. McRorie, A. Remanic, and D. Houston, *J. Am. Chem. Soc.*, **87**, 3246 (1965).